Synthesis and Fluorescence Properties of a Pyridomethene–BF$_2$ Complex
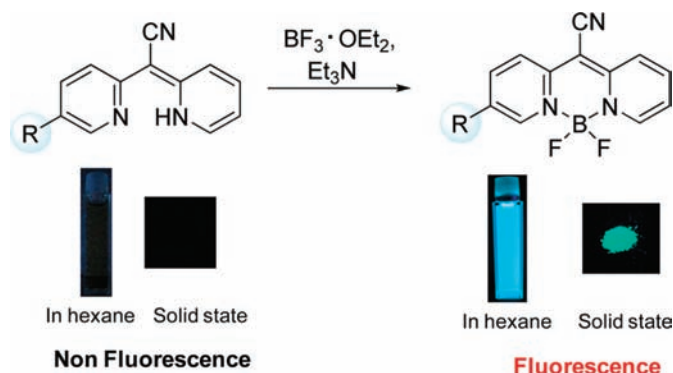
Yasuhiro Kubota,*,[†] Toshihiro Tsuzuki,[†] Kazumasa Funabiki,[†] Masahiro Ebihara,[‡] and Masaki Matsui*,[†]

Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan, and Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

kubota@gifu-u.ac.jp; matsuim@gifu-u.ac.jp

ABSTRACT

A fluorescent dye, the pyridomethene–BF$_2$ complex, has been synthesized. Although pyridomethenes did not exhibit fluorescence, pyridomethene–BF$_2$ complexes exhibited fluorescence both in solution and in the solid state. The trifluoromethyl-substituted BF$_2$ complex formed a J-aggregate and showed the highest fluorescence quantum yield in the solid state among all pyridomethene–BF$_2$ complexes.

Borondipyrromethene (BODIPY) dyes[1,2] are well-known fluorescent dyes with high fluorescence quantum yields, high extinction coefficients, sharp absorption and fluorescence emission spectra, and high photo- and chemical stability. Owing to these excellent characteristics, BODIPY dyes have a wide range of applications. They can be used in chemosensors,[3] in biolabels,[4] as sensitizers for dye-sensitized solar cells,[5] and as donor materials for bulk heterojunction solar cells,[6] as well as in photodynamic therapy.[7] However, most BODIPY dyes have defects such as very small Stokes shifts (5–20 nm,

in most cases) and high planarity.[8] These defects cause the self-quenching of BODIPY dyes in the solid state. Therefore, most BODIPY dyes hardly fluoresce in the solid state.[9]

[†] Department of Materials Science and Technology.

[‡] Department of Chemistry.

(1) (a) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891. (b) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1184.

(2) (a) Tram, K.; Yan, H.; Jenkins, H. A.; Vassiliev, S.; Bruce, D. *Dyes Pigm.* **2009**, *82*, 392. (b) Arroyo, I. J.; Hu, R.; Merino, G.; Tang, B. Z.; Peña-Cabrera, E. *J. Org. Chem.* **2009**, *74*, 5719. (c) Schmitt, A.; Hinkeldey, B.; Wild, M.; Jung, G. *J. Fluoresc.* **2009**, *19*, 755.

(3) (a) Móczár, I.; Huszthy, P.; Maidics, Z.; Kádár, M.; Tóth, K. *Tetrahedron* **2009**, *65*, 8250. (b) Guliyev, R.; Buyukcakir, O.; Sozmen, F.; Bozdemir, O. A. *Tetrahedron Lett.* **2009**, *50*, 5139. (c) Sekiya, M.; Umezawa, K.; Sato, A.; Citterio, D.; Suzuki, K. *Chem. Commun.* **2009**, 3047. (d) Sun, Z. N.; Wang, H. L.; Liu, F. Q.; Chen, Y.; Kwong, P.; Tam, H.; Yang, D. *Org. Lett.* **2009**, *11*, 1887. (e) Lee, H. Y.; Bae, D. R.; Park, J. C.; Song, H.; Han, W. S.; Jung, J. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 1239. (f) Coskun, A.; Akkaya, E. U. *J. Am. Chem. Soc.* **2005**, *127*, 10464. (g) Atilgan, S.; Ozdemir, T.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 4065. (h) Guliyev, R.; Coskun, A.; Akkaya, E. U. *J. Am. Chem. Soc.* **2009**, *131*, 9007.

(4) (a) Gonçalves, M. S. T. *Chem. Rev.* **2009**, *109*, 190. (b) Wang, D.; Fan, J.; Gao, X.; Wang, B.; Sun, S.; Peng, X. *J. Org. Chem.* **2009**, *74*, 7675.

(5) (a) Ertan-Ela, S.; Yilmaz, M. D.; Icli, B.; Dede, Y.; Icli, S.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 3299. (b) Hattori, S.; Ohkubo, K.; Urano, Y.; Sunahara, H.; Nagano, T.; Wada, Y.; Tkachenko, N. V.; Lemmetyinen, H.; Fukuzumi, S. *J. Phys. Chem. B* **2005**, *109*, 15368.

On the other hand, fluorescent boron complexes excluding BODIPY dyes have attracted considerable attention in recent times.[10] A pyridomethene−BF$_2$ complex is an analogue of a BODIPY dye. To the best of our knowledge, some papers[11] and some patents[12] have been published on the pyridomethene−BF$_2$ complex. However, the fluorescence properties of the complex have not been investigated in detail. In the present paper, we not only describe a convenient method for synthesizing the pyridomethene−BF$_2$ complex but also present its fluorescence properties.

BODIPY dyes are synthesized by the reaction of pyrromethene (dipyrrin)[13] with trifluoroborane. Therefore, it was supposed that pyridomethene would be a good precursor to the pyridomethene−BF$_2$ complex. Pyridomethene is an enamine tautomer of bis(2-pyridyl)methane (Figure S1, Supporting Information (SI)). Because of the aromatic stability of the pyridine ring, pyridomethene mostly exists in the imine form, i.e., bis(2-pyridyl)methane.[14] However, several reports have described the synthesis of meso-cyano-

substituted pyridomethene derivertives.[15] The findings of these reports indicate that the introduction of a cyano group at the meso position is an effective way to stabilize the pyridomethene structure. Our DFT calculations support these experimental results (Figure S2, SI). We chose meso-cyano-substituted pyridomethene derivatives as the precursor because they are easy to obtain and they enable the retention of the pyridomethene structure.

meso-Cyano-substituted pyridomethene 1 was obtained by the reaction of 2-(cyanomethyl)pyridine with 2-bromopyridine (Scheme S1, SI).[15b] The pyridomethene structure of 1 was confirmed by the ^{1}H NMR signal at δ 16.3 (brs, 1H, D$_2$O exchangeable, NH) and ^{13}C NMR signal at δ 68.2 (s, meso-carbon atom) (Figures S3, S4, SI). The observed symmetrical ^{1}H and ^{13}C NMR spectra indicate that the rate of interconversion between 1 and 1′ is faster than the NMR time scale (Figure S5, SI). The rapid interconversion between 1 and 1′ can be attributed to an imine−enamine tautomerism and/or a direct hydrogen shift between two nitrogen atoms in the vinamidine conjugate system. A similar symmetric property in the NMR spectrum was reported for another pentacyclic amidine (vinamidine).[16]

The reaction of 1 with boron trifluoride diethyl ether complex in the presence of triethylamine yielded the pyridomethene−BF$_2$ complex 5 (Scheme 1). The structure

(6) (a) Rousseau, T.; Cravino, A.; Bura, T.; Ulrich, G.; Ziessel, R.; Roncali, J. Chem. Commun. 2009, 1673. (b) Rousseau, T.; Cravino, A.; Bura, T.; Ulrich, G.; Ziessel, R.; Roncali, J. J. Mater. Chem. 2009, 19, 2298.
(7) (a) Ozlem, S.; Akkaya, E. U. J. Am. Chem. Soc. 2009, 131, 48. (b) Erbas, S.; Gorgulu, A.; Kocakusakogullaric, M.; Akkaya, E. U. Chem. Commun. 2009, 4956. (c) Atilgan, S.; Ekmekci, Z.; Dogan, A. L.; Guc, D.; Akkaya, E. U. Chem. Commun. 2006, 4398. (d) Gorman, A.; Killoran, J.; O'Shea, C.; Kenna, T.; Gallagher, W. M.; O'Shea, D. F. J. Am. Chem. Soc. 2004, 126, 10619.
(8) Small Stokes shift causes the reabsorption of its own fluorescence, so the fluorescence intensity was decreased. High planarity leads to increasing intermolecular interactions which cause concentration quenching.
(9) (a) Zhang, D.; Wen, Y.; Xiao, Y.; Yu, G.; Liu, Y.; Qian, X. Chem. Commun. 2008, 4777. (b) Hepp, A.; Ulrich, G.; Schmechel, R.; Seggern, H.; Ziessel, R. Synth. Met. 2004, 146, 11. (c) Ozdemir, T.; Atilgan, S.; Kutuk, I.; Yildirim, L. T.; Tulek, A.; Bayindir, M.; Akkaya, E. U. Org. Lett. 2009, 11, 2105.
(10) (a) Wakamiya, A.; Mori, K.; Yamaguchi, S. Angew. Chem., Int. Ed. 2007, 46, 4273. (b) Zhou, Y.; Xiao, Y.; Chi, S.; Qian, X. Org. Lett. 2008, 10, 633. (c) Zhou, Y.; Xiao, Y.; Li, D.; Fu, M.; Qian, X. J. Org. Chem. 2008, 73, 1571. (d) Nagai, A.; Kokado, K.; Nagata, Y.; Arita, M.; Chujo, Y. J. Org. Chem. 2008, 73, 8605. (e) Maeda, H.; Mihashi, Y.; Haketa, Y. Org. Lett. 2008, 10, 3179. (f) Ono, K.; Hashizume, J.; Yamaguchi, H.; Tomura, M.; Nishida, J.; Yamashita, Y. Org. Lett. 2009, 11, 4326. (g) Inokuma, Y.; Easwaramoorthi, S.; Yoon, Z. S.; Kim, D.; Osuka, A. J. Am. Chem. Soc. 2008, 130, 12234. (h) Kovalska, V. B.; Volkova, K. D.; Manaev, A. V.; Losytskyy, M. Y.; Okhrimenko, I. N.; Traven, V. F.; Yarmoluk, S. M. Dyes Pigm. 2010, 84, 159. (i) Yoshino, J.; Kano, N.; Kawashima, T. J. Org. Chem. 2009, 74, 7496. (j) Takeuchi, Y.; Matsuda, A.; Kobayashi, N. J. Am. Chem. Soc. 2007, 129, 8271. (k) Fischer, G. M.; Krondahl, M. I.; Schnetmann, I. G.; Daltrozzo, E.; Zumbusch, A. Chem.−Eur. J. 2009, 15, 4857. (l) Feng, J.; Liang, B.; Wang, D.; Xue, L.; Li, X. Org. Lett. 2008, 10, 4437. (m) Wu, L.; Burgess, K. J. Am. Chem. Soc. 2008, 130, 4089. (n) Maeda, H.; Haketa, Y.; Nakanishi, T. J. Am. Chem. Soc. 2007, 129, 13661. (o) Inokuma, Y.; Yoon, Z. S.; Kim, D.; Osuka, A. J. Am. Chem. Soc. 2007, 129, 4747. (p) Liddle, B. J.; Silva, R. M.; Morin, T. J.; Macedo, F. P.; Shukla, R.; Lindeman, S. V.; Gardinier, J. R. J. Org. Chem. 2007, 72, 5637. (q) Yoshino, J.; Kano, N.; Kawashima, T. Chem. Commun. 2007, 559. (r) Kobayashi, N.; Takeuchi, Y.; Matsuda, A. Angew. Chem., Int. Ed. 2007, 46, 758.
(11) (a) Douglass, J. E.; Barelski, P. M.; Blankenship, R. M. J. Heterocycl. Chem. 1973, 10, 255. (b) Scheibe, G.; Daltrozzo, E.; Wörz, O.; Heiss, J. Z. Phys. Chem. N.F 1969, 64, 97. (c) Basting, D.; Schäfer, F. P.; Steyer, B. Appl. Phys. 1974, 3, 81.
(12) Vargas, J. R.; Kondakov, D. Y. US Pat. 2005270204.
(13) Wood, T. E.; Thompson, A. Chem. Rev. 2007, 107, 1831.
(14) (a) Dyker, G.; Muth, O. Eur. J. Org. Chem. 2004, 4319. (b) Niwa, T.; Yorimitsu, H.; Oshima, K. Org. Lett. 2007, 9, 2373. (c) Dyker, G.; Muth, O. Eur. J. Org. Chem. 2004, 4319. (d) Zhang, J.; Khaskin, E.; Anderson, N. P.; Zavalij, P. Y.; Vedernikov, A. N. Chem. Commun. 2008, 3625. (e) Zheng, Z.; Elmkaddem, M. K.; Fischmeister, C.; Roisnel, T.; Thomas, C. M.; Carpentier, J.-F.; Renaud, J. -L. New J. Chem. 2008, 32, 2150.

Scheme 1. Synthesis of Pyridomethene−BF$_2$ Complexes

1: R = H
2: R = Br
3: R = CH$_3$
4: R = CF$_3$

5: R = H
6: R = Br
7: R = CH$_3$
8: R = CF$_3$
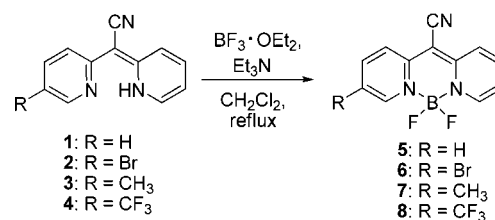
of 5[17] was confirmed by NMR spectra and X-ray crystallographic analysis (Figure S6, SI). The UV−vis absorption and fluorescence spectra of 1 and 5 in hexane are shown in Figure 1. The UV−vis absorption spectra of 5 showed two absorption peaks at 319 and 450 nm along with vibrational peaks at 306 and 425 nm, respectively. The weak absorption peak at 319 nm and the strong absorption peak at 450 nm can be attributed to an S$_0$→S$_2$ transition and an S$_0$→S$_1$ transition, respectively.

Although 1 did not show any fluorescence, 5 exhibited fluorescence at 456 nm in hexane. The difference between

(15) (a) Krämer, R.; Fritsky, I. O. Eur. J. Org. Chem. 2000, 3505. (b) Newkome, G. R.; Joo, Y. J.; Evans, D. W.; Pappalardo, S.; Fronczek, F. R. J. Org. Chem. 1988, 53, 786. (c) Newkome, G. R.; Joo, Y. J.; Theriot, K. J.; Fronczek, F. R. J. Am. Chem. Soc. 1986, 108, 6074.
(16) (a) Kubota, Y.; Satake, K.; Ikui, R.; Okamoto, H.; Kimura, M. Bull. Chem. Soc. Jpn. 2003, 76, 805. (b) Knorr, R.; Weis, A. Chem. Ber. 1981, 114, 2104.
(17) Although compound 5 was reacted with HCl aq or NaOH aq in THF at room temperature for 3 days, decomposition of 5 was not observed. Therefore, pyridomethene−BF$_2$ complexes are considered to be comparatively stable against acid and base.
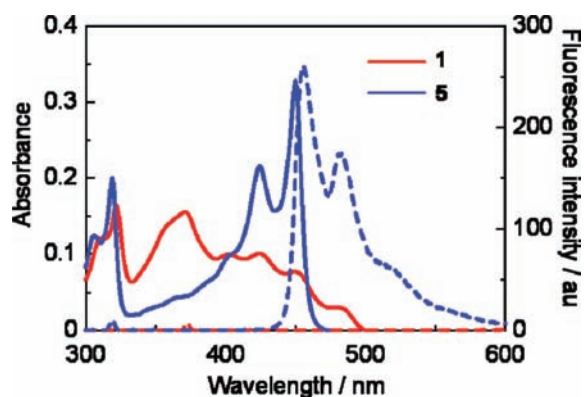
Figure 1. UV−vis absorption and fluorescence spectra of **1** and **5** in hexane. Measured at a concentration of 1×10^{-5} mol dm^{-3} of substrate at 25 °C. Solid and dotted lines represent UV−vis absorption and fluorescence spectra, respectively.

Table 1. Optical Properties of Pyridomethene−BF$_2$ Complexes

compd	R	hexane[a]			solid state[c]	
		λ_{max} ($\varepsilon \times 10^{-4}$) / nm	F_{max} /nm	$\phi_f{}^b$	F_{max} (nm)	$\phi_f{}^b$
5	H	319 (2.0), 450 (3.3)	456	0.19	503	0.03
6	Br	326 (2.3), 451 (2.4)	473	0.03	513	0.02
7	CH$_3$	320 (1.8), 456 (3.2)	461	0.19	504	0.04
8	CF$_3$	321 (2.3), 453 (3.2)	460	0.17	524	0.17
9	(Me-phenyl)	324 (2.2), 458 (4.8)	465	0.25	507	0.04
10	(Me,Me-phenyl)	323 (2.2), 456 (4.4)	463	0.18	496	0.12
11	(F$_3$C-phenyl)	324 (2.0), 456 (4.7)	463	0.18	496	0.06
12	(naphthyl)	325 (1.9), 459 (4.4)	468	0.18	512	0.08

[a] Measured at a concentration of 1.0×10^{-5} mol dm^{-3} at 25 °C. [b] Determined using a Hamamatsu Photonics Absolute PL Quantum Yield Measurement System C9920-02. [c] Excitation wavelength (λ_{ex}) was obtained by measuring the diffuse reflectance spectra given in Kubelka−Munk units.

the fluorescence properties of **1** and **5** can be attributed to the increase in rigidity of the pyridomethene skeleton of **5** caused by the chelation by the boron atom. This reduced the loss of energy via radiationless thermal vibrations.[1b,18] Compound **5** showed a very small Stokes shift (6 nm). The absorption and fluorescence properties of **5** in various solvents were investigated (Figures S7, S8 and Table S1, SI). The absorption and fluorescence maxima of **5** were only slightly affected by solvent polarity. The fluorescence of **5** can be observed in any solvent ($\phi_{toluene} = 0.30$, $\phi_{CH2Cl2} = 0.29$, $\phi_{THF} = 0.29$, $\phi_{CHCl3} = 0.27$, $\phi_{EtOH} = 0.27$, $\phi_{MeCN} = 0.26$, $\phi_{MeOH} = 0.26$, $\phi_{hexane} = 0.19$).

A similar procedure for 2-(cyanomethyl)pyridine with 2,5-dibromopyridine, 2-bromo-5-methylpyridine, and 2-bromo-5-trifluoromethylpyridine gave *meso*-cyano-substituted pyridomethenes **2**, **3**, and **4**, respectively (Scheme S1, SI). Compounds **6**−**8** were synthesized by the reaction of the corresponding pyridomethene with the boron trifluoride diethyl ether complex (Scheme 1). Aryl-substituted pyridomethene−BF$_2$ complexes **9**−**12** were also synthesized by the Suzuki−Miyaura cross-coupling reaction (Scheme S2, SI). The absorption and fluorescence properties of **5**−**12** in hexane are shown in Table 1 and Figures S9 and S10 (SI). It was observed that the absorption and fluorescence maxima of pyridomethene−BF$_2$ complexes were only slightly affected by the substitution of the aryl group. Although all pyridomethene−BF$_2$ complexes exhibited fluorescence in hexane, the bromo derivative **6** exhibited a relatively low fluorescence quantum yield (0.03) when compared with the other compounds (0.17−0.25). This difference in quantum yield may be attributed to the heavy-atom effect, which causes an intersystem crossing to a nonradiative triplet state.[19]

It is interesting to note that all the synthesized pyridomethene−BF$_2$ complexes exhibited fluorescence in the solid state, whereas most BODIPY dyes did not exhibit

fluorescence in the solid state.[9] This is a significant difference between the pyridomethene−BF$_2$ complexes and the BODIPY dyes. The solid-state fluorescence spectra of pyridomethene−BF$_2$ complexes are shown in Figure S11 (SI). In the solid state, these compounds exhibited fluorescence maxima and fluorescence quantum yields in the range of 496−524 nm and 0.02−0.17, respectively (Table 1). In aryl-substituted compounds **9**−**12**, fluorescence quantum yield increased as the substituent group was hindered. The trifluoromethyl-substituted derivative **8** showed the highest fluorescence quantum yield (0.17). The fluorescence quantum yield of **8** was identical in both the hexane solution and the solid state, whereas the fluorescence quantum yields of other compounds in the solid state were lower than in solution.

To investigate the difference in the solid-state fluorescence properties of each compound, X-ray crystallographic analysis was performed for compounds **5** ($\phi_f = 0.03$) and **8** ($\phi_f = 0.17$). In the crystal structure of **5**, the boron atom (B1) is in the same plane containing atoms N1, N2, C5, C6, and C7, and the molecule has an almost planar structure (Figure S6, SI). The crystal packing is shown in Figure S12 (SI) and Figure 2. As shown in Figure 2, the blue molecules and red molecules are arranged in a columnar fashion. Significant intermolecular π−π interactions were observed between the blue molecules and the red molecules. The intermolecular π−π interactions link the neighboring molecules and result in the formation of network π−π interactions. The π−π interactions are known to cause fluorescence quenching in

(18) Ikeda, C.; Ueda, S.; Nabeshima, T. *Chem. Commun.* **2009**, 2544.
(19) Gorman, A.; Killoran, J.; O'Shea, C.; Kenna, T.; Gallagher, W. M.; O'Shea, D. F. *J. Am. Chem. Soc.* **2004**, *126*, 10619.
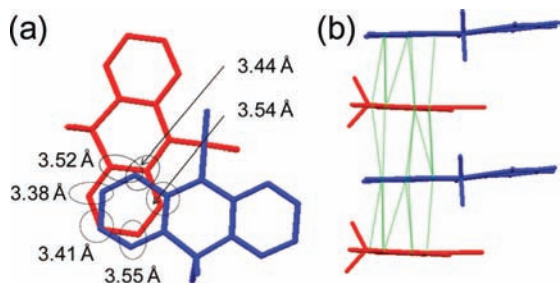
Figure 2. Crystal packing of **5**: (a) top view and (b) side view of **5**. Hydrogen atoms have been omitted for clarity. The dotted lines represent intermolecular C⋯C and C⋯N interactions.

the solid state.[20] Hence, it can be supposed that compound **5** shows a lower fluorescence quantum yield.

The ORTEP drawing of **8** is shown in Figure S13 (SI), and its crystal packing is shown in Figure S14 (SI) and Figure 3. In the crystal structure of **8**, the boron atom (B1) is slightly
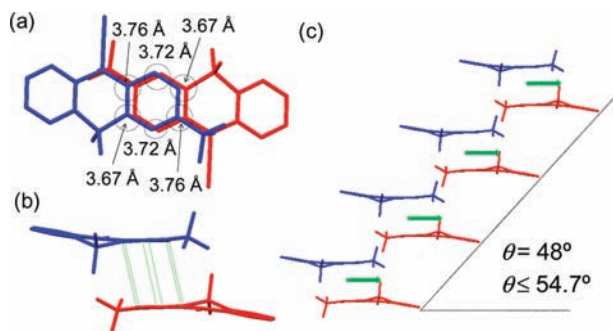

Figure 3. Crystal packing of **8**: (a) top view, (b) side view, and (c) stacking of **8**. Hydrogen atoms have been omitted for clarity. The dotted lines represent intermolecular C⋯C and C⋯N interactions. The green arrows indicate the transition dipole moment.

out of the plane that contains atoms N1, N2, C5, C6, and C7, and as a result, the molecule appears slightly bent. As in the case of compound **5**, networks of $\pi-\pi$ interactions were observed in the crystal of **8**. Surprisingly, despite the existence of $\pi-\pi$ networks, compound **8** exhibited strong fluorescence in the solid state. The packing patterns of compounds **5** and **8** are considerably different from each other. X-ray crystallographic results revealed that compound

8 formed a dimer in the crystal (Figure 3). The transition dipole moment of the dimer was determined by a TDDFT calculation at the B3LYP/6-31G(d,p) level (Figure S15, SI). The dimers are arranged head to tail along the transition dipole moment (Figure 3). The corresponding angle between two transition dipole moments is 48°. According to the excitation interaction model,[21] these results indicate that compound **8** forms a typical J-aggregate.

It is known that the formation of a J-aggregate causes bathochromic shifts of the absorption and fluorescence spectra.[21] To confirm the formation of the J-aggregate of **8**, the effect of the concentration of the substrate in the range of $10^{-6}-10^{-2}$ M on the fluorescence and excitation spectra was examined in dichloromethane. Because the concentrations were too high to measure the absorption spectra, the excitation spectra were measured instead (Figures S16, S17, SI). As the concentration increased from 10^{-6} to 10^{-2} M, red shifts were observed in both the fluorescence and the excitation spectra. These results suggest that compound **8** forms a J-aggregate in the concentrated state. It has been reported that the formation of a J-aggregate leads to an increase in the fluorescence intensity.[22] Therefore, because of the formation of the J-aggregate, it is likely that **8** may show the highest fluorescence quantum yield in the solid state.

In conclusion, we have synthesized a pyridomethene−BF$_2$ complex by the reaction of pyridomethene with boron trifluoride and investigated its fluorescence properties both in solution and in the solid state. All the synthesized pyridomethene−BF$_2$ complexes exhibited fluorescence in solution. The fluorescence quantum yields of the complexes were in the range of 0.03−0.25 in hexane solution. Furthermore, the complexes exhibited solid-state fluorescence. The fluorescence maximum and fluorescence quantum yield were in the range of 496−524 nm and 0.02−0.17, respectively. It was observed that the fluorescence quantum yield of these complexes tended to increase in the solid state as the substituent group became more sterically hindered. In addition, a trifluoromethyl-substituted derivative formed a J-aggregate and showed an exceptionally high fluorescence quantum yield in the solid state.

Supporting Information Available: Details of experimental procedures and copies of ^{1}H, ^{13}C NMR, and 2D spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL101612Z

(20) (a) Matsui, M.; Ikeda, R.; Kubota, Y.; Funabiki, K. *Tetrahedron Lett.* **2009**, *50*, 5047. (b) Shimizu, M.; Takeda, Y.; Higashi, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 3653.

(21) Kasha, M.; Rawls, H. R.; Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371.
(22) (a) Kaiser, T. E.; Wang, H.; Stepanenko, V.; Würthner, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 5541. (b) An, B. K.; Kwon, S. K.; Jung, S. D.; Park, S. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14410.